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Block 13: Supplementary Note

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Mercury cadmium selenide for infrared detection

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I. INTRODUCTION

Currently, the infrared material of choice is mercury cadmium telluride (MCT). MCT is a ternary alloy with a bandgap that can be tuned from the short wave infrared (SWIR) to the very long wave infrared (VLWIR). High quality MCT can be grown via molecular beam epitaxy (MBE) on bulk lattice-matched cadmium zinc telluride (CZT), with dislocation densities $\sim 10^5$ cm⁻². However, bulk CZT has a maximum area of roughly 50 cm², making it unsuitable for the manufacture of a large area focal plane array (FPA). MCT can also be grown by MBE on silicon (Si) with a cadmium telluride (CdTe) buffer layer. Si wafers are available in diameters at least as large as 10 in., but the 19% lattice mismatch between MCT and Si results in large dislocation densities that limit device performance, particularly for long wave infrared (LWIR) MCT.¹

An alternative material is mercury cadmium selenide (MCS). Like MCT, MCS is a ternary alloy with a bandgap tunable from the SWIR to the VLWIR. MCS belongs to a family of materials with lattice parameters near 6.1 Å. GaSb, another member of this family, is now available in wafers with a diameter of 4 in., with 6 in. diameter GaSb wafers currently under development. Additionally, this 6.1 Å family also includes materials with band gaps suitable for detection applications in the visible and ultraviolet spectral ranges. Therefore, one could conceivably create a device made from lattice-matched materials capable of sensing from the ultraviolet to the VLWIR on a single chip.²

One obstacle to the use of MCS for devices has been the large background electron concentration that has been reported for this material. Despite not being intentionally doped, MCS samples typically had electron concentrations greater than 10^{17} cm⁻³ at 77 K whether in the form of bulk samples³ or of epitaxial layers deposited by MBE.⁴ The electron concentration remained high with little variation even at temperatures as low as 4 K, suggesting the presence of a shallow donor level located near or within the conduction band. The background concentration could either be reduced or increased by annealing under various conditions, suggesting the presence of native defects such as vacancies and interstitials.⁵ Sources of these donor defects need to be identified so that a process to eliminate them either during growth or through postgrowth annealing can be developed.

II. EXPERIMENT

MCS samples were grown via MBE on Si substrates with zinc telluride (ZnTe) buffer layers.⁶ The samples were grown in an ultrahigh vacuum MBE chamber made by DCA Instruments. The substrates were mounted on molybdenum blocks with colloidal graphite. Immediately prior to loading, the ZnTe/Si substrates were etched in a 0.2% Br:Methanol solution for 30 s followed by a brief methanol rinse, a 10 s etch in 10% HCl, a 60 s rinse in deionized water, and then blown dry with N₂. Once loaded, the substrate was heated under a Te overpressure while monitored *in situ* by reflection high energy electron diffraction to remove any remaining oxides prior to growth. Clips held the edges of each substrate, and the thickness (and therefore the growth rate) of

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each sample could be determined by measuring the “step” created by the clip with a profilometer.

MCS samples were grown using elemental mercury (Hg), cadmium (Cd), and selenium (Se) sources. The beam equivalent pressure (BEP) emanating from all sources was measured with a beam flux monitor (BFM) consisting of a nude ion gauge placed directly in the path of flux. Quadruple distilled Hg was supplied by a 600cc valved effusion cell and Cd with 99.999% (5N) purity was supplied by a 400g SUMO Cell, both made by Applied EPI. Initially, a Model VSb110 effusion cell made by ADDON was used to supply 5N Se. However, Se vapor consists of many polyatomic species from Se_2 to Se_8 , and at this effusion cell's typical operating temperature of 325 °C (598 K), the predominant species of Se flux was Se_6 (uncracked Se).⁷

The Se effusion cell was replaced with a Mark V Selenium Valved Cracker made by Veeco, which directed the Se vapor through a cracking zone, which could be heated up to 800 °C (1073 K) to produce a predominantly Se_2 beam (cracked Se).^{7,8} Differences in the ionization efficiencies of the Se atomic species resulted in different sensitivities of the BFM depending on which species were dominant. For a fixed reservoir temperature of 250 °C and a fixed valve position (to maintain a constant flux), the BEP measured for the cracker source was found to vary with the cracking zone temperature, tracking with the data found in Ref. 7. This suggests that the Se flux transitions from predominantly Se_6 to predominantly Se_5 at around 650 K and then to predominantly Se_2 near 900 K (Fig. 1). The Se BEP measured for the typical cracking zone temperature of 800 °C was found to be close to a factor of two lower than at the typical effusion cell temperature of 325 °C for the same amount of exiting Se reflecting a difference in ionization energy for the various species. This correction factor was applied to Se BEP from the cracker source when comparing the two sources. While the effusion cell was loaded with 5N purity Se, the cracker was loaded with Se with 99.9999% (6N) purity.

Samples were grown at different temperatures using various Cd to Se and Hg to Se BEP ratios. Substrate temperature was measured with a pyrometer as well as a thermocouple on

the sample manipulator. However, samples grown using the cracker source presented some difficulty in measuring the substrate temperature. Heat from the high temperature cracking zone was reflected off the substrate into the pyrometer, making it more difficult to obtain an accurate measurement. An estimate of substrate temperature was determined comparing thermocouple and pyrometer temperature readings.

Cut off wavelength was determined via transmittance measurements using a Fourier transform infrared spectroscopy and the molar fraction of CdSe in the MCS alloy, or x -value, was determined from this measurement using the relationship between band gap and x -value developed by Summers and Broerman.⁹ Hall measurements were performed over a range of temperatures from 4 to 300 K, on samples subjected to various postgrowth anneals. Finally, secondary ion mass spectroscopy (SIMS) was performed by the Charles Evans Analytical Group.

III. RESULTS AND DISCUSSION

A. Growth parameters

Due to the very low sticking coefficient of Hg, samples were grown with large Hg BEPs ($\sim 10^{-4}$ Torr). For a fixed substrate temperature and Hg overpressure, the growth rate varies linearly with Se BEP (Fig. 2), and for a fixed Se BEP, the x -value can be controlled by the Cd/Se BEP ratio (Fig. 3). It was found that samples grown with cracked Se had a higher x -value than samples grown with uncracked Se with the same Cd/Se ratio, suggesting greater incorporation of Cd with Se_2 than Se_6 . Growth rates began to decrease at approximately 130 °C for the valved source and 150 °C for the cracker source (Fig. 4). The optimal MBE substrate temperature for MCS grown with an Hg BEP of 2.5×10^{-4} Torr was ~ 100 °C. This is lower than the optimal temperature for MCT with a similar Hg BEP (~ 185 °C), most likely due to the higher vapor pressure of Se compared to Te.

B. Hall measurements

The electron concentration versus temperature was measured for samples grown with both Se sources using Hall

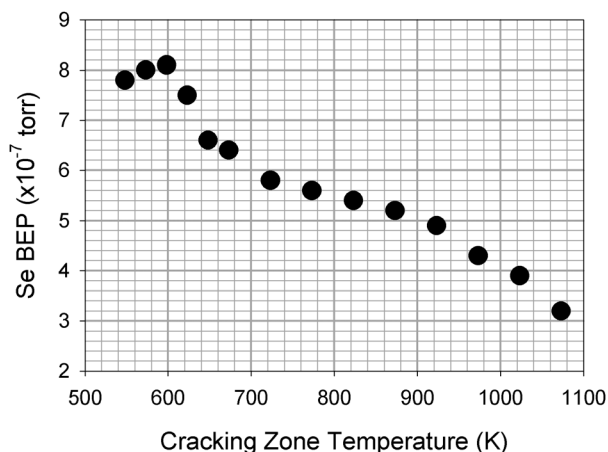


FIG. 1. Se BEP vs cracking zone temperature for a fixed Se reservoir temperature of 250 °C and valve position of 150 mils.

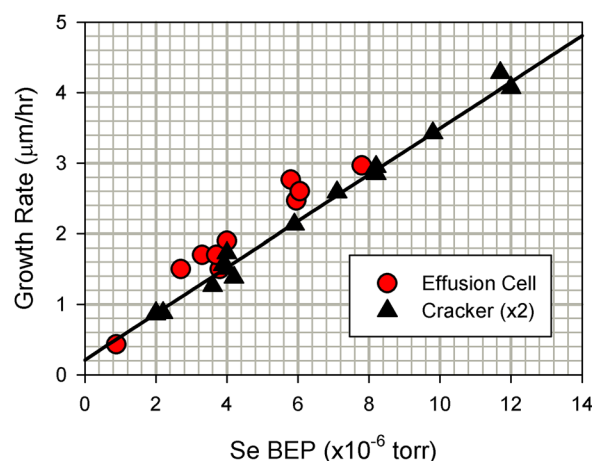


FIG. 2. (Color online) Growth rate vs Se BEP for both the effusion cell (Se_6) and the cracker source (Se_2).

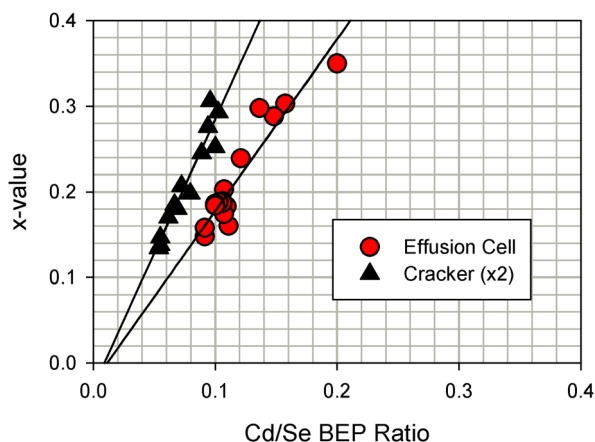


Fig. 3. (Color online) Cd composition vs Se/Cd BEP ratio for both the effusion cell (Se_6) and the cracker source (Se_2).

Effect measurements with a standard magnetic field of 0.1 T. A previous study of MCS grown via MBE using uncracked Se reported little variation in electron concentration with temperature below 100 K, with the electron concentration remaining in the 10^{17} – 10^{18} cm^{-3} range at temperatures as low as 30 K.⁴ This was consistent with samples grown by the effusion cell, but MCS samples grown with the cracker source exhibited a temperature dependency with as-grown 12 K electron concentrations in the 10^{16} – 10^{17} cm^{-3} range (Fig. 5). The relative lack of carrier freeze-out and the lower electron concentrations with the cracker source suggest the presence of donors with energy levels located near or within the conduction band that were significantly reduced by switching to the Se cracker source.

Two differences between the Se effusion cell vs the Se cracker source that could explain the lower electron concentrations are the different atomic species of the Se beam ($\sim\text{Se}_6$ vs $\sim\text{Se}_2$) and the higher purity source material in the cracker source (5 N vs 6 N). MCS samples were grown using the 6 N Se in the cracker source, with the cracking zone temperature lowered to 325 °C to produce an uncracked predominantly Se_6 beam. The electron concentration remained low even when the cracking zone temperature was reduced to

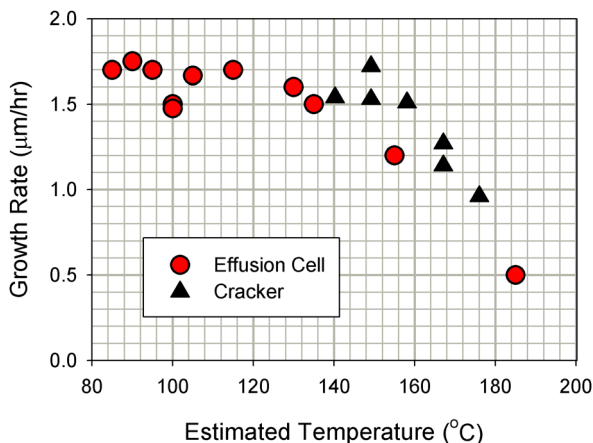


Fig. 4. (Color online) Growth rate vs estimated substrate temperature with a fixed Se BEP for both the effusion cell (Se_6) and the cracker source (Se_2).

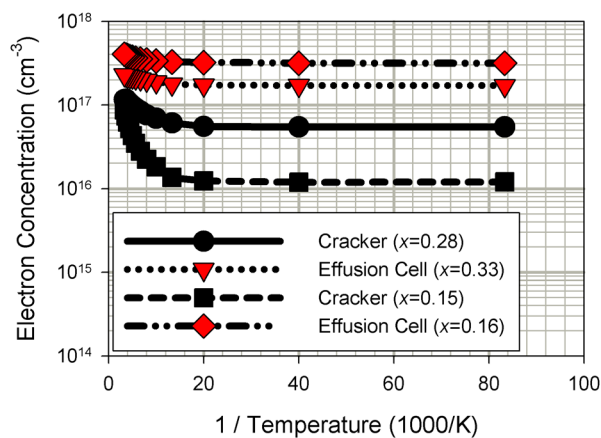


Fig. 5. (Color online) As-grown electron concentration vs temperature for MCS samples grown with both Se sources.

325 °C (Fig. 6), strongly suggesting that the reduction in concentration was due to the higher purity source material and not the predominantly Se_2 flux. Electron mobility for the MCS samples increased as the x -value decreased (Fig. 7).

A prior study of HgSe annealed under Hg and Se suggested that Hg interstitials (n-type), Se vacancies (n-type), and Hg vacancies (p-type) were possible native defects in MCS.⁵ These possibilities were investigated by subjecting MCS samples to separate 24 hour, 250 °C anneals under vacuum, a Hg overpressure, a Cd overpressure, or a Se overpressure in sealed quartz ampoules. The electron concentration always increased when annealed under Hg or Cd, and the electron concentration was reduced for samples grown with the cracker source and then annealed under Se. No significant changes were observed for samples annealed under vacuum (Fig. 8). RBS measurements indicated an increase in x -value when annealed under Cd, but no significant change in composition with the other anneals.

The lowest 12 K electron concentration achieved was for a Se-annealed sample with an x -value of 0.15. The as-grown 12 K concentration of $1.2 \times 10^{16} \text{ cm}^{-3}$ was reduced to $9.4 \times 10^{15} \text{ cm}^{-3}$ after annealing under Se. Overall, switching

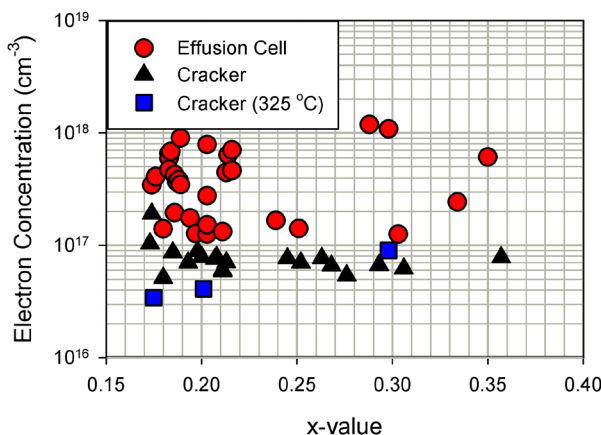


Fig. 6. (Color online) As-grown electron concentration at 77 K vs x -value for the effusion cell (Se_6), the cracker source at typical operating temperatures (Se_2), and cracker source with the cracking zone temperature at 325 °C (Se_6).

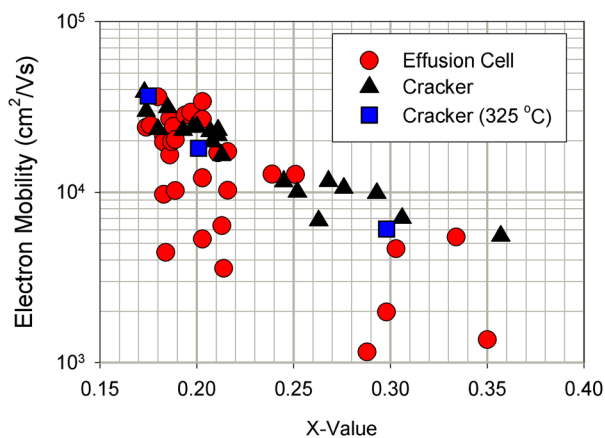


FIG. 7. (Color online) As-grown electron mobility at 77 K vs x -value for the effusion cell (Se_6), the cracker source at typical operating temperatures (Se_2), and cracker source with the cracking zone temperature at 325 °C (Se_6).

to the higher purity Se and then annealing under a Se overpressure typically reduced the background electron concentration by an order of magnitude at 77 K. Direct studies of vacancies and interstitials are being performed through positron annihilation spectroscopy and Rutherford backscattering channeling spectroscopy, respectively. These results will be presented at a later date.

C. SIMS measurements

SIMS measurements were conducted on an MCS sample grown with the effusion cell (thickness = 7.3 μm), an MCS sample grown with the cracker source (thickness = 3.5 μm), and a HgSe sample grown with the effusion cell (thickness = 3.4 μm) in order to identify unintentional impurities (Fig. 9). For all three samples, group VII elements such as Br, Cl, and F were detected at the interface with the ZnTe buffer layer. Br and Cl could be introduced during the substrate preparation process and could serve as n-type dopants

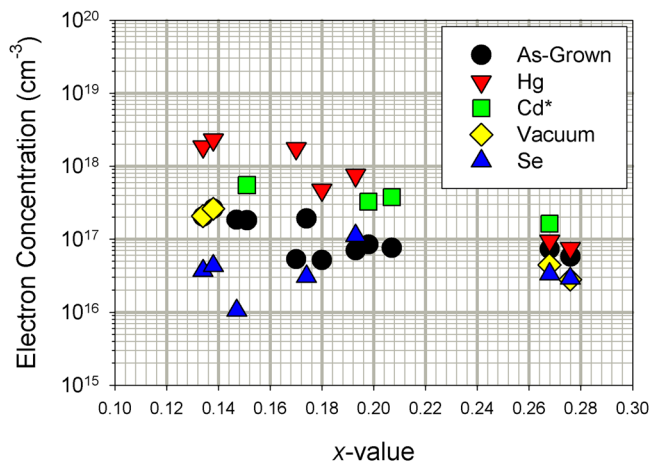


FIG. 8. (Color online) 77 K electron concentration both as-grown and after annealing under various overpressures of Hg, Se, Cd, and under vacuum. All anneals were performed in quartz ampoules pumped down to $\sim 10^{-5}$ Torr, then sealed and kept in a furnace at 250 °C for 24 h, followed by a 3 h cool-down. * x -value listed is prior to annealing.

if they substituted group VI Se lattice sites. C and O were detected in a region approximately 1.5 μm thick at the surface of the MCS and at the interface between MCS and ZnTe. The source of these impurities and whether they are electrically active in MCS needs to be established. Two other contaminants listed in the Cd source material certificate of analysis were group VI S and group IV Si, both of which were detected in all samples but significantly reduced in the HgSe sample where the Cd source was not

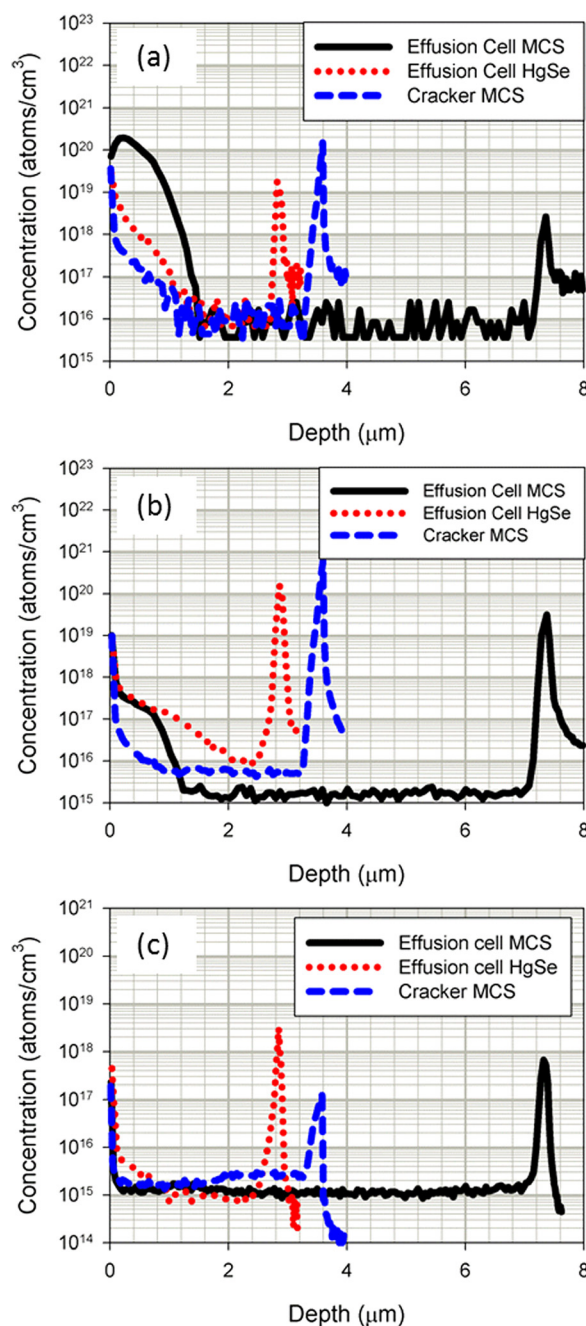


FIG. 9. (Color online) SIMS results of a MCS sample grown with the effusion cell (thickness = 7.3 μm), MCS sample grown with the cracker source (thickness = 3.5 μm), and an HgSe sample grown with the effusion cell (thickness = 3.4 μm) for (a) carbon (b) oxygen and (c) bromine. SIMS measurements were performed by the Charles Evans Analytical Group.

used—strongly suggesting they are contaminants in the Cd source material.

Unfortunately none of the SIMS measurements to date have differed significantly between the MCS samples grown with the 5N and 6N Se source material, and so the impurities that were reduced by switching to higher purity Se source material have yet to be identified.

IV. SUMMARY AND CONCLUSIONS

MCS samples were grown via MBE on ZnTe/Si substrates using two different Se sources: an effusion cell loaded with 5N source material that produced a predominantly Se_6 beam and a cracker source loaded with 6N source material that could be varied to study other Se polyatomic species. Samples grown with the Se_2 had greater x -values with lower Cd/Se BEP ratios, suggesting greater Cd incorporation with Se_2 . The growth rate began to decrease when the substrate temperature was raised above $\sim 130^\circ\text{C}$ under an Se_6 flux and $\sim 150^\circ\text{C}$ under an Se_2 flux. The optimal substrate temperature for MCS grown with the effusion cell was found to be $\sim 100^\circ\text{C}$ for an Hg BEP of 2.5×10^{-4} Torr—lower than the optimal temperature for MCT growth with a similar Hg overpressure ($\sim 185^\circ\text{C}$).

Electron concentrations remained high even at low temperatures, with as-grown 12 K concentrations ranging from 10^{17} to 10^{18}cm^{-3} for samples grown with 5N Se source material and 10^{16} – 10^{17}cm^{-3} for samples grown with 6N Se. Impurities can produce energy levels located in the conduction band of narrow-gap materials, such as In dopants in MCT. As a result, these impurities do not freeze-out at lower temperatures and the concentration remains high even at temperatures as low as 4 K.¹⁰ The fact that the electron concentration remains high in MCS even at low temperatures indicates the presence of energy levels in the conduction band similar to MCT, and the fact that the 12 K concentration was lower for 6N Se strongly suggests that impurities are introduced from contaminants in the Se source material.

SIMS measurements detected impurities which could be acting as donors, the most prevalent of which was C. Br and Cl were detected at the MCS/ZnTe interface, suggesting they could be introduced by the substrate preparation process. Significant levels of C and O were detected at the MCS/ZnTe interface and in the top $1.5\text{ }\mu\text{m}$ of the MCS layer from the surface. Further measurements are required to determine how these impurities are introduced, whether they are electrically active, and how they can be eliminated.

The MCS electron concentration could also be changed by postgrowth annealing. Anneals under Hg and Cd overpressures raised the electron concentration, while anneals under Se or vacuum lowered the electron concentration. This would suggest the presence of native defects such as interstitials and vacancies in addition to the background impurities. The identity of these native defects and an annealing process to eliminate them is currently under investigation.

If MCS is to be used for LWIR applications, the background electron concentration needs to be reduced to at most $\sim 10^{15}\text{cm}^{-3}$ (assuming a similar lifetime to MCT). Switching from 5N Se to 6N Se reduced the electron concentration from 10^{17} – 10^{18}cm^{-3} to $3\text{--}5 \times 10^{16}\text{cm}^{-3}$, suggesting that the background concentration could be further reduced by using 7N or higher purity Se source material. Further study of native defects present in MCS is required so that a process for removing them through postgrowth annealing can be optimized. Once the background electron concentration has been fully minimized, p-type doping of MCS can be developed so that MCS device layers can be produced.

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